Class- and Structure-Specific Separation, Analysis, and Identification Techniques for the Characterization of the Sulfur Components of JP-8 Aviation Fuel

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Methods have been described for separating the sulfur content of aviation fuels into chemical classes for identification and quantitation. These separation methods simplified the fuel matrix, which allowed non-element-specific detection methods, such as mass spectrometry (MS), to be used for sulfur detection. These matrix simplification methods also enhanced the ability of element-specific detection methods, such as atomic emission detection (AED), to identify sulfur species that are present in the fuel. Separation of a model fuel mixture, as well as several representative aviation fuels, was performed using several different methods, including class-specific chemical oxidation methods that used iodine and another that used hydrogen peroxide, and a polarity-based separation that used a polar high-pressure liquid chromatography (HPLC) column. Following separation, sulfur concentration was quantified into "reactive" and "non-reactive" classes, on the basis of the ease of transformation of the species, using chemical oxidation procedures, which also relates to the tendency for the species to undergo typical hydrodesulfurization reactions with hydrogen. These two classes were broken down further, with sulfur compounds being classified as thiol, sulfides and disulfides, thiophenes, benzothiophenes, or dibenzothiophenes. The separation and identification methods proved to be robust and transferable; the results from two independent laboratories were in good agreement. Sulfur in the jet fuels tested in this study appeared mainly as thiols, sulfides, and disulfides, as determined by gas chromotography−atomic emission detection (GC−AED), following the chemical oxidation procedures. Of the refractory sulfur compounds, benzothiophenes comprised the majority, as determined by GC−MS following the (HPLC) fractionations. Thiophenes and dibenzothiophenes contributed minor amounts to the total concentration of refractory sulfur compounds. Two main components of the benzothiophene class were identified to be 2,3-dimethyl benzothiophene and 2,3,7-trimethyl benzothiophene.

Introduction

The sulfur content of distillate fuels continues to come under more stringent regulation by the U. S. Environmental Protection Agency (EPA) and other environmental regulatory agencies worldwide. Of primary concern is the sulfur poisoning of advanced automotive catalysts that are used to reduce emissions of pollutant hydrocarbons, carbon monoxide, and nitrogen oxides from gasoline- and diesel-fueled vehicles. Sulfur emissions from the combustion of a wide range of distillate fuels also present environmental concerns, because they contribute to acid rain.[1-8] Tier II sulfur regulations

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mandate that sulfur levels in gasoline be reduced from the current level of 300 ppm to 30 ppm by 2004, whereas sulfur levels in on-road diesel fuel must be reduced from 500 ppm to 15 ppm by 2006.[9−11]

The next transportation fuel that may likely be subjected to more-stringent sulfur regulations is aviation fuel, which currently has a total sulfur limit of 3000 ppm. Anticipation of lower limits for sulfur in aviation fuels has raised several concerns, with respect to how the fuel will behave under the high stresses that the fuel typically encounters, as well as the performance of engines that are powered by this fuel. In advanced aircraft that are used in military applications, jet fuel is used as a heat-exchange fluid to cool the airframe, engines, and avionics. Under the stress of high temperature, jet fuel can form oxidative deposits as the fuel thermally degrades. These carbonaceous deposits can decrease fuel flow, which, in turn, can lead to severe degradation of aircraft performance, loss of airframe subsystems, and even catastrophic failure of jet engines. Previous research has shown that the formation of thermal deposits is greatly affected by the sulfur concentration of the fuel.[12−14] Other fuel characteristics, such as lubricity and storage stability, are also dramatically affected by the amount of sulfur in the fuel, in both positive and negative ways.[15]

Simultaneous with jet engine development, the chemical composition of petroleum-derived jet fuels has been studied in an attempt to understand how the chemical composition of the fuel affects engine performance. As a result of those studies, the formation of deposits in jet fuels under thermal stress has been associated with the presence of reactive sulfur species such as thiols, sulfides, and disulfides. Just as deposit formation can be attributed to certain classes of sulfur compounds, the ease of removal of sulfur compounds from distillate fuels is also class dependent. For example, under certain conditions for hydrodesulfurization, the most reactive and easiest-to-remove classes of sulfur compounds are thiols, sulfides, and disulfides; compounds such as substituted benzothiophenes and dibenzothiophenes are more difficult to remove.[1,3,6,16−18] Therefore, it may be practical to alter fuel performance by targeting the removal of certain classes of sulfur compounds.

Before conducting additional studies to link the structure and reactivity of sulfur compounds in jet fuel, methods must be developed for determining the concentrations of individual classes of sulfur compounds, along with further identification of the individual components that comprise these classes. The methods must be robust enough to determine trace levels of sulfur components within a large hydrocarbon matrix. Although methods currently exist for measuring the total sulfur and thiol/mercaptan sulfur concentration of distillate fuels, routine methods for measuring the total nonreactive and reactive sulfur species in those fuels may be more informative. Although regulatory requirements only necessitate quantification of the total amount of sulfur present, it is clear that speciated sulfur information is necessary for a better understanding of the fuel properties and performance characteristics.

The analysis of sulfur in aviation fuel and other transportation fuels has been performed with both specific and universal detectors. The use of gas chromatography (GC) with sulfur-specific detectors, such as atomic emission detection (AED) and flame photometric detection (FPD), as well as the Hall detector, is well documented for isolation of individual sulfur components in distillate fuels.[1,7,19−23] Sulfur-specific detection allows for simplification of the fuel chromatogram by detection of only the hydrocarbons that contain sulfur. However, assignment of the peaks in the sulfur chromatogram to individual sulfur-containing species is still complicated and laborious, because it necessitates a comparison of the retention times of hundreds of sulfur compound peaks with those of known standards of appropriate purity. If the matrix effects from the hydrocarbon sample can be eliminated by other means, it may be more convenient to use a universal detection method, such as mass spectrometry (MS), to identify unknown sample components.[24,25] Separating the target analytes from the matrix also may enhance the capabilities of the other detectors.

Giddings[26] and others involved in multidimensional separations recognized that separation power need not be limited to one technique. Liquid chromatography− gas chromatography (LC−GC), supercritical fluid extraction−gas chromatography (SFE−GC), and other sample preparation techniques that are combined with GC are appropriate and powerful applications of multidimensional separations.[27] The work described herein includes a preseparation procedure that uses high-pressure liquid chromatography (HPLC) to isolate some of the important sulfur-containing species in jet fuels for mass spectral interpretation. The work also includes other wet chemical methods for class-specific separation and quantitation of sulfur species in jet fuels. The recovery of sulfur compounds from these wet chemical

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Table 1. Conditions Used for Sulfur-Specific Analysis of Class-Separated Samples by GC–AED

	laboratory 1	laboratory 2
column	DB-1701 (Supelco); 30 m, 0.32 mm i.d., 1.0 μm df; 14% cyanopropylphenyl, 86% dimethylpolysiloxane	Rtx-1 (Restek); 30 m, 0.32 mm i.d., 4.0 μm df; 100% dimethylpolysiloxane
inlet	helium carrier, 17 psi head pressure (constant), 280 °C inlet temperature; 1 μL injection volume, 20:1 split ratio	
oven	40 °C for 1 min, 40 °C to 250 °C @ 2.0 °C/min	
detector	sulfur emission, 181 nm; transfer line, 280 °C makeup gas, 100 mL/min; cavity temperature, 280 °C	

methods was explored, and potential losses of target species during the oxidation steps were identified. In addition, standards bracketing and the retention times of standard sulfur compounds are used to identify the major components of jet fuels, as measured by GC–AED. The standards bracketing method allows a higher degree of accuracy for class determinations than a simple subtraction of "before and after" sulfur chromatograms. Simple subtraction of full chromatograms would introduce significant errors in sulfur determinations, because oxidized sulfur species that are not completely removed by the chemical process would appear in the chromatogram, which would bias the results.

The advantages of these methods include the ability to separate the sulfur components in a jet fuel (JP-8) on the basis of structural class and/or ring number, allowing both sulfur-specific and universal detection methods to be used. The methods also allow the identification of several of the major individual sulfur compounds within these classes. This work provides a more comprehensive collection of methods for initially elucidating the identity and concentration of sulfur compounds that are present in jet fuel, to enable future studies that will link the sulfur-compound structure to fuel properties and reactivity.

Experimental Section

Samples. The samples used in this study were various Jet A and Jet A-1 fuels that have undergone different degrees of hydrotreatment. Therefore, the fuels are representative of jet fuels that may be encountered under actual scenarios, with sulfur concentrations ranging from high sulfur concentrations (>1300 ppm) to lower sulfur concentrations (<400 ppm). A standard reference material—SRM 1616a, sulfur in kerosene (NIST, Gaithersburg, MD)—was used to verify calibration.

A model mixture of sulfur compounds in fuel was prepared by spiking known amounts of several pure sulfur-containing compounds into a zero-sulfur kerosene. The mixture contained thiols, sulfides, disulfides, thiophenes, and benzothiophenes at a relatively low total sulfur level of ~165 μg/mL (see Table 4, presented later in this work). A portion of this mixture was diluted in zero-sulfur kerosene to yield a second standard that had a total sulfur content of ~83 μg/mL. These standard mixtures were used to evaluate the completeness of removal of the target species by the class-selective oxidation procedures.

Wet Chemical Class Separations. To characterize specific classes of sulfur compounds in the fuel samples, a procedure by Stumpf et al. was utilized.[18] The method was slightly modified to include retention indices, to distinguish the sulfur classes. In this procedure, sulfur class type is determined by oxidizing the reactive sulfur species, thiols, sulfides, and disulfides, followed by analysis of the sulfur-containing compounds by GC–AED. Thiols in the fuel are selectively oxidized with iodine, and subsequent phase separation leaves the original sulfides and thiophenic compounds untouched. Hydrogen peroxide selectively oxidizes the thiols, sulfides, and disulfides to form sulfonic acids and sulfones, which are

removed by phase separation, leaving the thiophenic compounds unreacted.

Briefly, for the iodine oxidation, 3 mL of each fuel was mixed with 3 mL of iodine solution (0.32 g of I_2 in 8 mL of acetone). After periodic shaking for 10 min at room temperature, 2 mL of sodium thiosulfate solution (0.8 g of $Na_2S_2O_3$ in 10 mL of 0.05 M NaOH) was added. Phases were separated, and the fuel layer was washed four times with 2-mL portions of 18 MΩ·cm water. For the peroxide oxidation, 3 mL of 30% H_2O_2 was added to 3 mL of the fuel, along with 1 mL of acetic acid and 1 mL of acetone. The mixture was maintained at 60 °C for 1 h and was vigorously shaken periodically. Phases were separated, and the fuel layer was washed four times with 2-mL portions of 18 MΩ·cm water. More specific procedural details are available in the literature.[18]

Sulfur analyses of raw fuels and oxidized fractions were conducted in two different laboratories. One laboratory used a Hewlett–Packard model HP-5890 gas chromatograph that was equipped with an auto-sampler (Agilent, model 7673 ALS) that was coupled to an atomic emission detector (Agilent, model 2350A). The other laboratory used an Agilent model 6890A gas chromatograph with an Agilent model 7683 ALS auto-sampler, coupled to an Agilent model 2350A atomic emission detector. The details for chromatographic separation and emission detection are given in Table 1.

For instrument calibration, a three-component standard mixture was prepared by dissolving three different sulfur compounds, each at different concentrations, in sulfur-free kerosene (Fisher Scientific). Portions of this three-component mixture were further diluted with sulfur-free kerosene to create two additional calibration mixtures. Each mixture was injected, thus performing external calibration for a range of nine different sulfur concentrations using only three injections. This technique has been previously described and verified.[28] All calibration mixtures, standard reference materials, and fuel samples were injected and analyzed according to the details given in Table 1.

Standards Bracketing Method. The retention information gained from hydrocarbon standards was used to segment the different sulfur-containing classes that are present in the fuels. To determine their retention times, the following bracketing standard compounds were injected into the GC–AED system: benzene, naphthalene, phenanthrene, and chrysene. Conditions were as given in Table 1, except that, unlike the sulfur analyses, the carbon 179 emission line was monitored by AED to detect the elution of these standards.

HPLC Fractionation. The HPLC system (Agilent, model 1100) used a normal-phase cyano-column (Zorbax-CN, Agilent Technologies), along with detectors for diode-array detection (DAD) and refractive index detection (RID) used in series. Experimental details for the HPLC fractionation procedure are described in Table 2. Aviation fuels were first diluted to 100:1 in hexane and injected into the chromatographic system. Using a mobile phase of n-hexane (Fisher Scientific), the complex mixtures were separated into compound classes on the basis of polarity. These compound classes were detected by DAD and RID measurement at low concentrations for chromatographic resolution. After retention times for the classes had been established, subsequent separations were conducted by manual

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Table 2. Instrumental Conditions for HPLC Fractionations and GC−MS Analysis

HPLC separation conditions		GC−MS analysis conditions	
mobile phase	*n*-hexane	carrier gas	He
column	Zorbax-CN (Agilent), 4.6 mm × 15 cm	column	HP-1 (Agilent), 30 m × 0.25 mm i.d.
flow rate	0.5 mL/min	film thickness	0.25 μm
temperature	25 °C	injector	280 °C, splitless
fraction collection	manual	solvent delay	5.0 min
injection volume	40 μL	oven	40 °C (2 min) to 280 °C (3 min) at 5 °C/min

Table 3. List of Organo-sulfur Compounds Injected as Part of the Study to Identify Sulfur Compounds by Matching Retention Times[a]

compound class	thiophene	benzothiophene	dibenzothiophene
parent compound	thiophene	benzothiophene	*dibenzothiophene*
alkyl constituent	3-methyl	2-methyl	3-methyl
		3-methyl	2,4,6-trimethyl
		2,3-dimethyl	1,2,3,4-tetrahydro
		2,5-dimethyl	1,2,3,4,4a,4b-hexahydro
		3,7-dimethyl	
		3,5-dimethyl	
		7-ethyl	
		2-ethyl	
		2,3,7-trimethyl	
		2,5,7-trimethyl	
		2-ethyl-7-methyl	
		2-ethyl-5-methyl	
		2-propyl	
		2,3,4,7-tetramethyl	
		2-ethyl-5,7-dimethyl	
		2-propyl-7-ethyl	
		2,7-diethyl	

[a] Identified compounds are shown in italics.

collection of fractions from more-concentrated samples (20:1 dilution) without using the RI detector, which had high dead volume and caused significant peak dispersion.

The success of the fractionation was evaluated using the raw collected samples in *n*-hexane. Samples were not concentrated by evaporation, because of the potential to lose a high concentration of volatile alkyl benzenes in the aromatic fraction of the sample. To determine which fractions contained a majority of the sulfur compounds, portions of each of the collected fractions were analyzed for sulfur content by GC−AED. The "diaromatics" fraction (i.e., the fraction that contained primarily substituted naphthalenes) was found to contain the majority of sulfur compounds. A concentrated sample of this fraction was subsequently prepared by performing 10 injections on the HPLC separation system, accumulating each target fraction, and finally concentrating the fraction by solvent evaporation. Finally, a high-resolution GC−MS system (Agilent Technologies, model 6890-5973) was used to analyze concentrated collections of the "diaromatics" fraction to determine structural information about the individual sulfur compounds that were contained in the fuel. Conditions for the high-resolution GC−MS analysis are shown in Table 2.

Identification by Comparison with Known Samples. Raw jet fuel samples were analyzed by GC−AED (using the Agilent Technologies model 6890 gas chromatograph, with the Agilent Technologies model 7683 autosampler, coupled to an Agilent Technologies model 2350A atomic emission detector) and by GC−MS (using the Agilent Technologies model 6890 gas chromatograph and the Agilent Technologies model 5973 mass spectrometer). The study had, at its disposal, a supply of more than 250 individual sulfur compounds. After a preliminary evaluation of the class-separation results, it was determined that the major individual sulfur-containing constituents were benzothiophenes. Therefore, individual samples of various benzothiophenes, covering many of the one-carbon- (C1), two-carbon- (C2), and three-carbon-(C3) substituted benzothiophenes, were chosen for comparison to the chromatograms of the jet fuel. In addition, several other compounds within the thiophene and dibenzothiophene classes were injected. A listing of many of the sulfur compounds injected

as part of this identification study is given in Table 3. These standards were typically dissolved in a solvent such as isooctane or toluene, at concentration levels in the range of 5−200 μg/mL. The retention times and detector response for the pure compounds were compared to the retention times of the sulfur components in the jet fuel chromatograms.

Analysis of Total Sulfur in Fuels. In addition to the aforementioned methods for determining class-specific sulfur concentrations, the total sulfur concentrations in selected fuels were determined. Several analytical methods were used for total sulfur determinations, including traditional analysis by GC−AED, as well as "fast" GC−AED,[28,29] and UV fluorescence (using ASTM Method D5453) by an independent laboratory.[30]

Results and Discussion

Class Separation of Sulfur Compounds in Jet Fuels. The sulfur components were placed in classes based on a combination of their response to oxidation reactions and a chromatographic peak bracketing routine. All the sulfur components that were oxidized by iodine were classified as thiols. The components that were not oxidized by iodine but were oxidized by hydrogen peroxide were classified as sulfides or disulfides. This combined group of oxidizable components was broadly designated as being "reactive" sulfur species. The sulfur components that were not oxidized by either iodine or hydrogen peroxide were classified as either thiophenes, benzothiophenes, or dibenzothiophenes, and, as a group, these components were broadly designated as being "nonreactive" sulfur species. Figure 1 compares the GC−AED sulfur chromatograms of a

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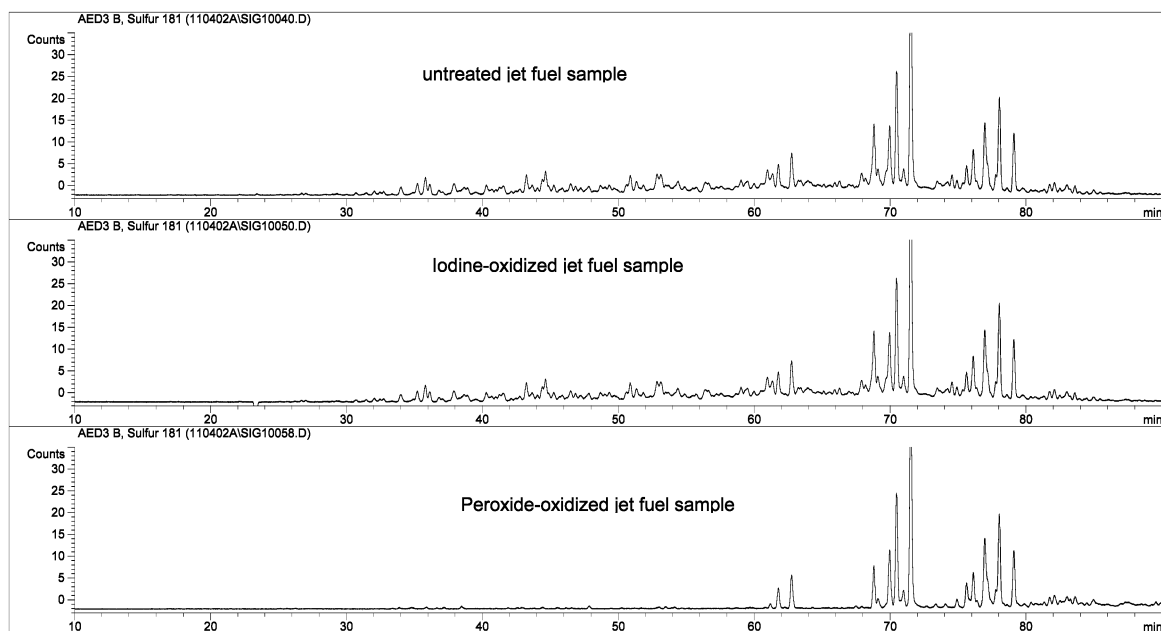
Figure 1. GC−AED sulfur chromatograms of an untreated sample of a representative jet fuel, an iodine-oxidized sample of the jet fuel, and a peroxide-oxidized sample of the jet fuel.
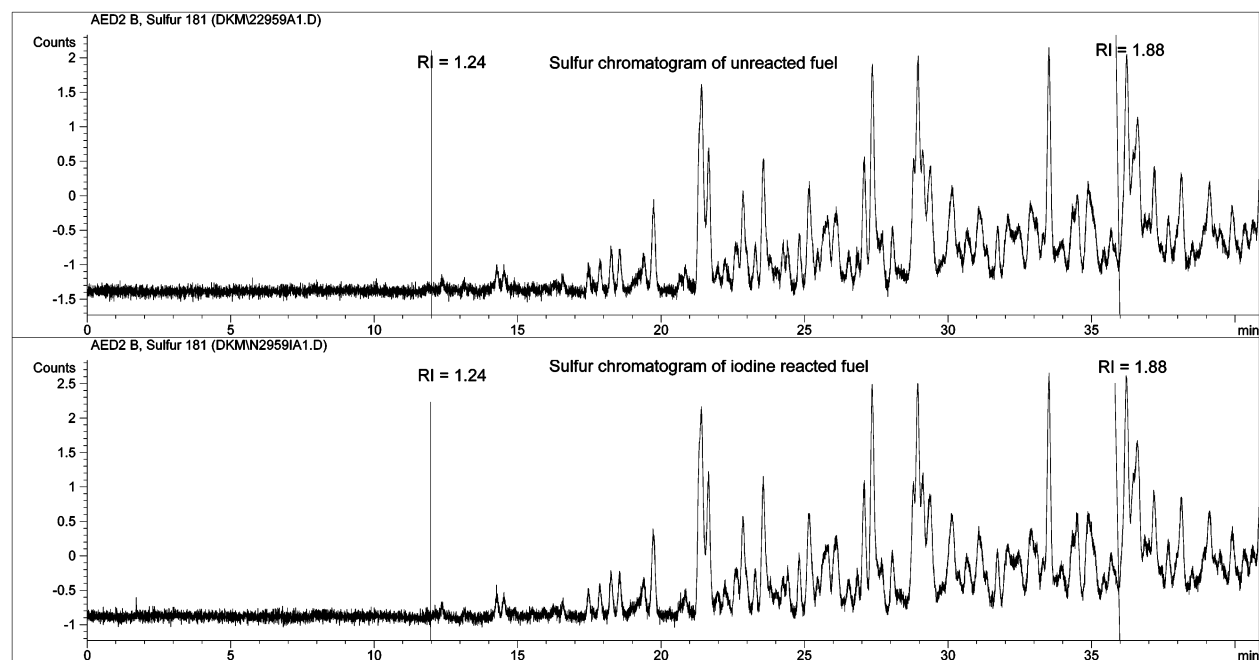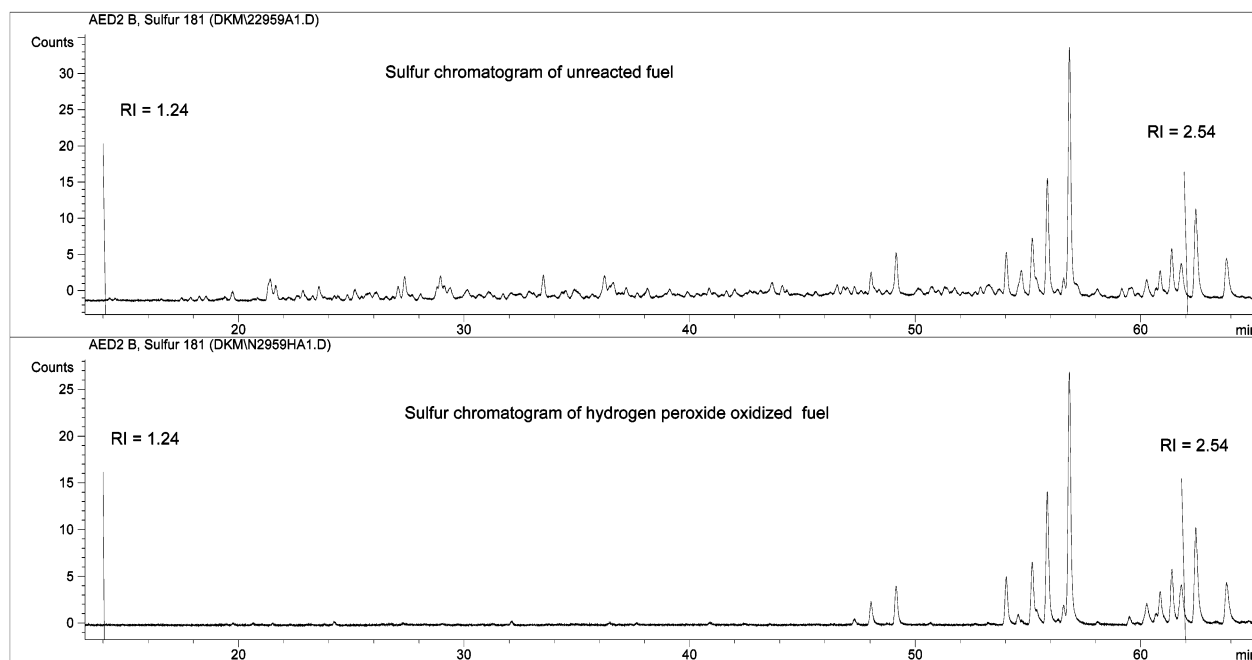

Figure 2. GC−AED sulfur chromatograms of the unreacted sample of jet fuel and the iodine-oxidized sample.

representative jet fuel sample with those of the iodine-oxidized and hydrogen peroxide-oxidized fuel samples.

For quantification of individual classes of sulfur species, the sulfur species were separated using segmented regions of the AED chromatograms that were based on the retention time of aromatic standards. Benzene was defined as having a retention index of RI = 1, naphthalene had a RI value of 2, phenanthrene had a RI value of 3, and chrysene had a RI value of 4. The concentration of thiols was determined by measuring the concentration of sulfur species with RI values of <1.88 units in the unreacted fuel, then subtracting from that the concentration of sulfur species with retention indices of <1.88 units in the iodine-oxidized fuel sample. An RI value of 1.88 was chosen because experimental results showed extraneous peaks in the

sulfur chromatogram of the iodine-oxidized samples that eluted after this RI value. Prior studies showed that thiols are the only species that were oxidized by iodine; therefore, the reduction in sulfur species observed in the iodine-oxidized fuel sample is attributed exclusively to the loss of thiol species. Figure 2 shows the AED chromatograms of the unreacted fuel and iodine-oxidized fuel sample, expanded about the region of RI = 1.88 units, to highlight the loss of thiol species. For the jet fuels tested in this study, the concentrations of thiols present were expected to be low; thus, the differences between the sulfur response for the untreated fuel and that of the iodine-oxidized fraction are slight.

Because thiols, sulfides, and disulfides are all oxidized by hydrogen peroxide, subtracting the concentration of

Figure 3. GC−AED sulfur chromatograms of the unreacted sample of jet fuel and the hydrogen peroxide-oxidized sample.

sulfur species with an RI value of <2.54 units in the hydrogen peroxide-oxidized fuel sample from the concentration of sulfur species within the same RI range in the unreacted fuel gave the combined concentration of the "reactive" sulfur species. To determine the concentration of the sulfide and disulfide fraction, the concentration of thiols, which was determined by the iodine oxidation, was subtracted from the concentration of "reactive" sulfur. The resulting concentration was classified as that of the sulfide and disulfide species. Figure 3 shows the AED chromatograms of the unreacted fuel and the hydrogen peroxide-oxidized fuel sample, expanded about the region of RI = 2.54 units, to highlight the loss of thiol, sulfide, and disulfide species. The large difference in sulfur response illustrates the large concentration of "reactive" sulfur compounds contained in this fuel.

The concentration of thiophenes was determined by measuring the combined concentration of sulfur species in the hydrogen peroxide-oxidized fuels with an RI value of <2.00 units, because thiophenes were the only sulfur species in this RI range that remained following hydrogen peroxide oxidation. The concentration of benzothiophenes was determined by measuring the combined concentration of sulfur species in the hydrogen peroxide-oxidized fuels with RI values of >2.00 units and <2.66 units. The concentration of dibenzothiophenes was determined by measuring the combined concentration of sulfur species in the unreacted fuel with RI values of >2.66 units and <3.54 units. The unreacted fuel chromatogram was used for dibenzothiophene quantitation, because the oxidized samples contain transformed sulfur species, such as sulfoxides and sulfones, which elute later in the chromatogram of oxidized fuels and could produce artificially high results for the dibenzothiophene concentration. Although oxidized sulfur species may be present in fuel, this peak bracketing routine may not be appropriate for their trace-level determination. These polar species would likely be partially removed by partitioning into the

aqueous oxidation solutions. Any remaining oxidized sulfur species would elute at retention times that correspond to benzothiophenes and dibenzothiophenes; however, their emission would be masked by the emission from the benzothiophenes and dibenzothiophenes, which would likely be present at much-higher concentrations.

To determine the transferability of the oxidation and peak grouping routine, the method was tested by a second laboratory using a different column for GC separation (as shown in Table 1). Because the separation was altered, retention times that correspond to the chosen RI values needed to be determined for the different column. To transfer the RI values to different separation conditions, retention times that corresponded to the specified RI values were determined. The bracket time was calculated according to the following equation:

$$\frac{rt_{bracket} - rt_{prevRI}}{rt_{nextRI} - rt_{prevRI}} = RI_{bracket} - RI_{prev}$$

where $rt_{bracket}$ is the desired retention time being calculated, rt_{prevRI} the retention time for the aromatic bracket standard that elutes prior to the desired retention index, rt_{nextRI} the retention time for the aromatic bracket standard that elutes after the desired retention index, $RI_{bracket}$ the desired retention index, and RI_{prev} the retention index for the aromatic bracket standard that elutes prior to the desired retention index. For the model DB-1701 column, benzene eluted at 4.0 min, whereas naphthalene eluted at 40.1 min; therefore, a bracket RI value of 1.88 corresponded to a retention time of 35.8 min. For the model Rtx-1 column, benzene and naphthalene eluted at 9.7 and 53.1 min, respectively; therefore, a retention time of 47.9 min corresponded to a bracket RI value of 1.88.

Spiked Sulfur Mixture Study. Jet fuels typically contain low levels of thiol species; thus, it was difficult to establish the effectiveness of the method for removal of this particular species. Therefore, a model fuel

Table 4. Recovery of Spiked Analytes from the Selective Oxidation of a Model Jet-Fuel Mixture

compound class	original concentration[a]	I$_2$-oxidized concentration	percent recovery	H$_2$O$_2$-oxidized concentration	percent recovery
		Fuel Containing 165.7 μg Total Sulfur/mL			
thiol	52.7 ± 0.32	nd[b]		nd[b]	
sulfide/disulfide	69.1 ± 0.41	60.6 ± 0.26	87.7 ± 0.65	nd[b]	
thiophene	17.1 ± 0.11	15.9 ± 0.09	93.5 ± 0.81	15.5 ± 0.12	90.6 ± 0.91
benzothiophene	26.8 ± 0.44	31.0 ± 0.12	115 ± 1.9	23.8 ± 0.08	89.0 ± 1.5
		Fuel Containing 83.6 μg Total Sulfur/mL			
thiol	26.4 ± 0.25	nd[b]		nd[b]	
sulfide/disulfide	34.4 ± 0.31	29.6 ± 0.12	85.9 ± 0.85	nd[b]	
thiophene	8.69 ± 0.103	8.05 ± 0.012	92.7 ± 1.1	7.73 ± 0.039	88.9 ± 1.1
benzothiophene	14.1 ± 0.04	16.0 ± 0.05	113 ± 0.5	11.8 ± 0.10	83.6 ± 0.75

[a] Concentrations expressed as μg sulfur/mL ± standard deviation; $n \geq 2$. [b] nd indicates that the species concentration was not detected, because of complete removal of the chromatographic peak of the target species.
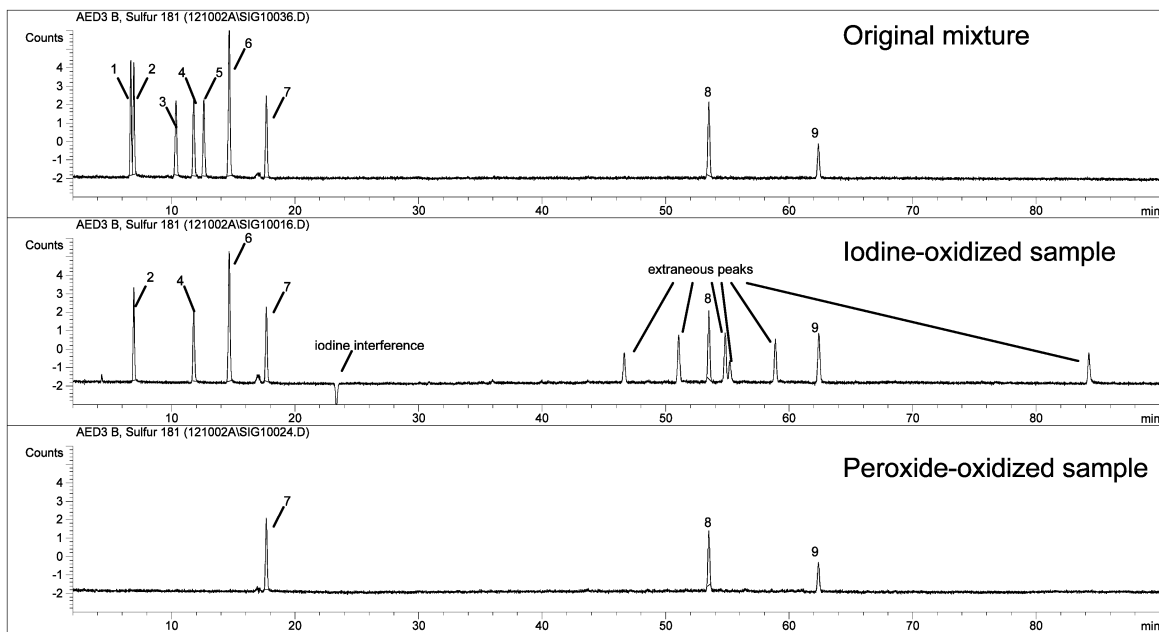
Figure 4. Sulfur chromatograms for the analysis of a model compound mixture, an iodine-oxidized sample, and a peroxide-oxidized sample, illustrating the removal of target classes by each oxidation procedure. Peak identities are as follows: 1, 1-propane thiol; 2, ethyl methyl sulfide; 3, 2-methyl-1-propane thiol; 4, diethyl sulfide; 5, 1-butane thiol; 6, methyl disulfide; 7, 3-methyl thiophene; 8, benzothiophene; and 9, 5-methyl benzothiophene.

mixture was prepared to test the ability of the method to selectively remove target classes of sulfur species at two different sulfur concentration levels. Using this model mixture, analytical parameters such as efficiency of removal, selectivity of oxidation, and sensitivity of the determination could be evaluated. Table 4 contains data regarding the removal and recovery of certain target fractions. Note the complete removal of thiols following the iodine oxidation procedure, as well as the complete removal of thiols, sulfides, and disulfides by the hydrogen peroxide oxidation procedure.

In addition to quantitative data, chromatographic evidence for the effectiveness of the oxidation procedure is shown in Figure 4. This figure shows the sulfur chromatogram for the original model fuel mixture, as well as those of the iodine-oxidized fuel mixture and the peroxide-oxidized fuel mixture. Complete removal of the three thiols was demonstrated by the iodine oxidation procedure, whereas other species remained in the mixture. For the peroxide-oxidized fraction, complete removal of thiols, sulfides, and disulfides was achieved, without the removal of thiophenes or benzothiophenes. It is important to note that the spiked thiol species appear at much shorter retention times than the region

where a response to sulfur emission is observed for samples of jet fuel that have been tested (shown in Figure 1). This observation indicates that these jet fuels do not contain significant quantities of thiols. Moreover, the overlay shows the rationale for choosing the endpoint for thiol elution at a RI value of 1.88. The iodine oxidation procedure converts thiols to more-polar sulfur compounds that elute after a RI value of 1.88. These compounds apparently are not completely removed via phase separation and washing. To minimize the introduction of positive bias, these extraneous peaks that result from the iodine oxidation procedure are excluded from the region of thiol quantification.

There were slight losses of thiophenes and benzothiophenes, as a result of the oxidation procedures. Although the magnitude of the losses is relatively small, they are repeatable. These losses may occur as a result of the processing of solutions during the oxidation procedure, because thiophenes and benzothiophenes are adsorptive and could be lost at each sample transfer step.[31] Loss of these species because of volatilization is

(31) Striebich, R. C.; Rubey, W. A.; Anderson, S. D. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1994**, *39*, 64−66.

Table 5a. Concentration of Sulfur,[a] As Determined by Sulfur Class-Separation Procedure by Independent Laboratories for Several Representative Jet Fuels

sample		thiols	thiols, sulfides, and disulfides	thiophenes	benzothiophenes	dibenzothiophenes
2827	Lab 1	19.2 ± 22.4	382 ± 46	6.4 ± 0.1	123 ± 26	56.8 ± 19.2
	Lab 2	2.0 ± 4.0	320 ± 12	12.8 ± 4.0	110 ± 5	118 ± 5
2926	Lab 1	3.2 ± 13	300 ± 28	nd[b]	46.4 ± 3.2	33.6 ± 6.4
	Lab 2	2.4 ± 2.1	236 ± 7	6.3 ± 2.1	58.9 ± 4.6	84.1 ± 2.9
2959	Lab 1	6.4 ± 14.4	832 ± 64	21.6 ± 4.8	422 ± 46	37.6 ± 1.6
	Lab 2	7.6 ± 10.0	793 ± 31	23.9 ± 1.0	513 ± 2.0	74.0 ± 2.2
3084	Lab 1	0.1 ± 9.6	343 ± 27	4.8 ± 1.6	114 ± 16	57.6 ± 4.0
	Lab 2	1.34 ± 5.84	323 ± 15	10.4 ± 2.5	124 ± 4	98.6 ± 2.1
3166	Lab 1	nd[b]	402 ± 34	8.0 ± 1.6	163 ± 2	55.2 ± 5.6
	Lab 2	1.14 ± 3.40	360 ± 8	14.2 ± 0.1	178 ± 2	97.4 ± 1.5

[a] Concentrations expressed as μg sulfur/mL $\pm$ standard deviation; $n \geq 2$. [b] nd indicates that the presence of this analyte was not detected using this method.

Table 5b. Total Concentration[a] of Sulfur in Fuels, Determined by Summation of Class Fractions, GC−AED Analysis of Untreated Fuel, and UV Fluorescence

sample	Sum of Fractions		GC−AED of Untreated Fuel		UV fluorescence of untreated fuel
	Lab 1	Lab 2	Lab 1	Lab 2	
2827	588 ± 60	560 ± 14	514 ± 6	667 ± 18	640 ± 10
2926	383 ± 32	385 ± 9	425 ± 28	465 ± 9	392 ± 8
2959	1319 ± 81	1404 ± 32	1307 ± 62	1428 ± 38	1307 ± 7
3084	519 ± 33	556 ± 16	559 ± 15	598 ± 17	543 ± 1
3166	626 ± 38	651 ± 8	673 ± 27	703 ± 10	652 ± 5

[a] Concentrations expressed as μg sulfur/mL $\pm$ standard deviation; $n \geq 2$.

also possible, especially when working with solutions at elevated temperatures, as in the hydrogen peroxide oxidation procedure. Further evidence that the losses are physical in nature is the absence of additional peaks in the target region of the sulfur chromatogram of the peroxide-oxidized mixture, indicating that additional sulfur species are not created during the oxidation procedure. The evaluation of the spiked mixture allowed us to conclude that the published method quantitatively removes the target species but may be susceptible to a slight loss of supposedly unreacted species. To our knowledge, this is the first time that the occurrence of losses using the published procedure[18] have been identified and quantified.

Table 5a shows a listing of the results for sulfur class separation and quantification for several representative fuels using the method that has been described. Table 5b compares the results obtained for total sulfur concentration by summing the fractions, as well as results of direct analysis of the untreated fuel by alternative methods. As the tables show, the summed results for the class-selective determinations are in agreement with the results for total sulfur concentration as determined by several different analytical techniques, showing good performance for the class-selective determinations. As mentioned previously, concentrations of thiols in hydrotreated fuels are expected to be low, so determinations using this method are more difficult as the level of thiols decreases. Regardless, note that consistent results are achieved for class determinations for independent laboratories using different chromatographic equipment, demonstrating that the selective oxidation and peak bracketing routine is transferable to different laboratories, using different chromatographic separation procedures.

Some interesting trends can be observed from the class-specific determinations. In all the fuels tested, the thiols, sulfides, and disulfides contribute more than 50% of the total sulfur concentration. This contribution seems to be independent of the total sulfur concentration of the fuel, because the fuel with the lowest sulfur concentration (sample 2926, with a total sulfur concentration of ~400 ppm) and the fuel with the highest sulfur concentration (sample 2959, with a total sulfur concentration of ~1300 ppm) both were composed of more than 60% thiols, sulfides, and disulfides. For the refractory sulfur compounds, the benzothiophene fraction was the majority, followed by dibenzothiophene, with thiophenes contributing less than 5% of the total sulfur in each jet fuel that was tested.

HPLC Class Fractionation. For additional speciation of the sulfur content in the fuel, the HPLC fractionation procedure isolated the fuel sample into the following different structural classes: saturates, single-ring compounds, double-ring compounds, and triple-ring compounds.[32] Ordinarily, the fuel matrix is too complex to use a nonselective detector, such as a mass spectrometer, to obtain good spectra for sulfur compounds. However, fractionation of the fuel into structural classes simplifies the matrix and allows GC−MS to be used as an effective tool for the detection and identification of various sulfur compounds in each fraction of the fuel.

The response of a refractive index detector was used to monitor the polarity separation of the compound classes in a typical kerosene-cut aviation fuel. The normal-phase HPLC separation proved to be a fast (<10 min) and convenient way to fractionate the sample of interest primarily into saturates, aromatics, and diaromatics fractions. GC−MS was used to confirm the initial measurements of the RID value and to evaluate the ability of the fractionation procedure to separate the desired fractions from each other accurately. The chromatogram for the neat fuel and the chromatograms for the saturates, aromatics, and diaromatics fractions are shown in Figure 5a, b, c, and d, respectively. Note that

(32) Striebich, R. C.; Rubey, W. A.; Klosterman, J. R.; Balster, L. M. T. Presented at the 23rd International Symposium on Capillary Chromatography and Electrophoresis, Las Vegas, NV, 2001.
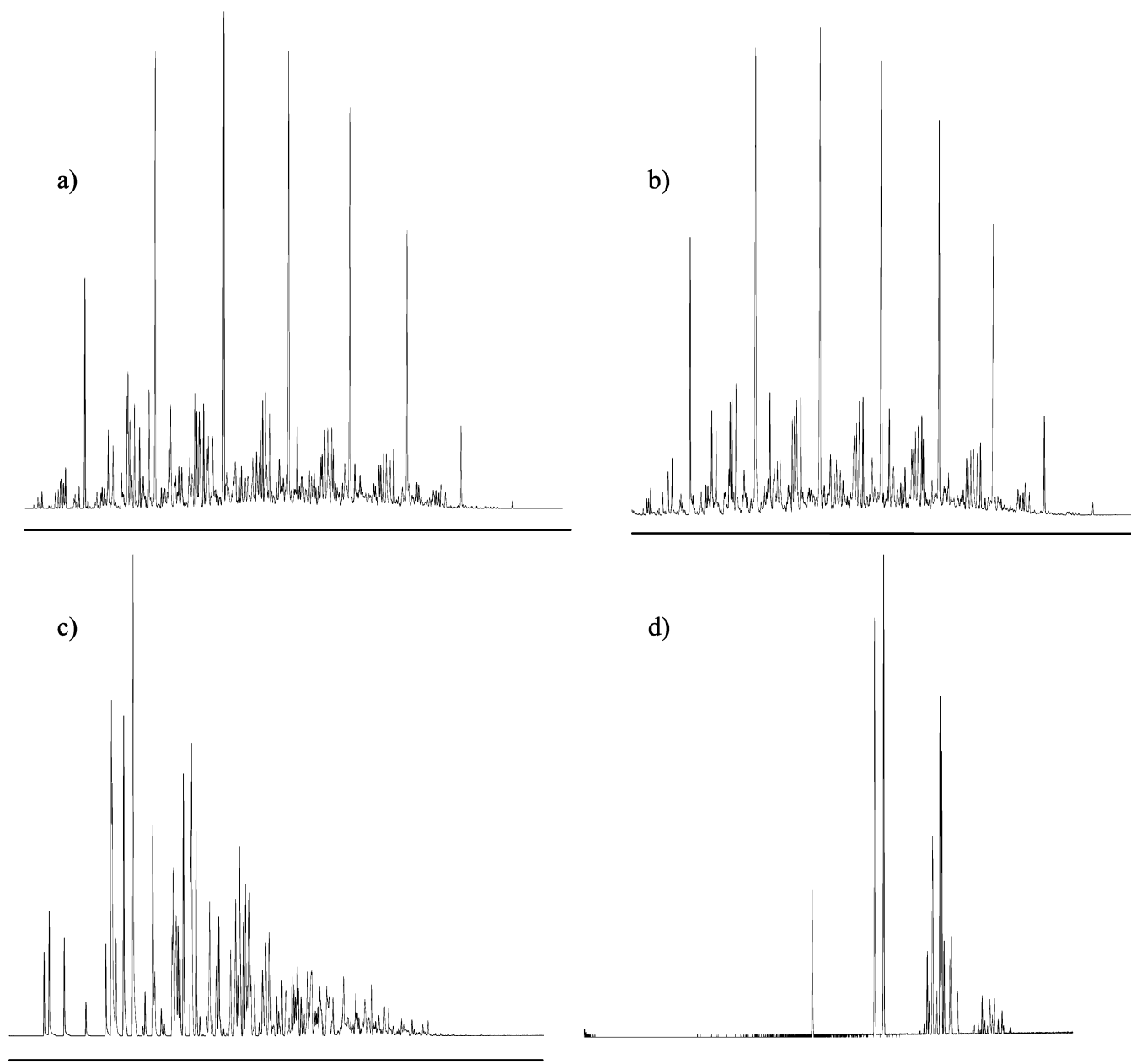
Figure 5. GC−MS chromatograms of (a) the raw fuel, (b) the HPLC fractionated saturates, (c) mono-aromatics, and (d) di-aromatics.

the figures are presented on dramatically different scales. Had identical scales been used, the chromatograms for the aromatic and diaromatic fractions would be obscured, because the saturates fraction comprises more than 75% of the fuel.

Carryover among the fractions was not observed, even between the saturates fraction and the aromatics fraction, even though the saturates fraction comprises more than 75% of the fuel matrix. Additional evidence for the robustness of the fractionation method is provided by the appearance of saturated dicycloalkanes (decalins) in the saturates fraction, whereas the unsaturated cycloalkanes (tetralins) were identified in the aromatics fraction. Further characterization of the fractions showed that the aromatic fraction consisted of C2- through C7-substituted benzenes primarily, whereas the diaromatics fraction contained naphthalene and C1- through C3-substituted naphthalenes. The polarity-sensitive normal

phase fractionation procedure was determined to have separated the classes of compounds in the fuel correctly.

To determine which of the fuel fractions contained the highest concentration of sulfur compounds, each fraction from a high-sulfur jet fuel was analyzed for sulfur via GC−AED. This sulfur-specific detector responds only to the sulfur compounds in the fuels, thus allowing determination of the distribution of sulfur-containing compounds among the HPLC-fractionated samples. The sulfur-specific chromatograms for each of these fractions are shown in Figure 6.

GC−MS scans were performed on the fractionated fuels, and then extracted ion chromatographs were obtained from the scans. Even though hydrocarbon species still comprised a majority of the fractionated matrixes, the fractionation procedure simplified the matrix enough to identify sulfur-containing species. A majority of the sulfur-containing compounds were present
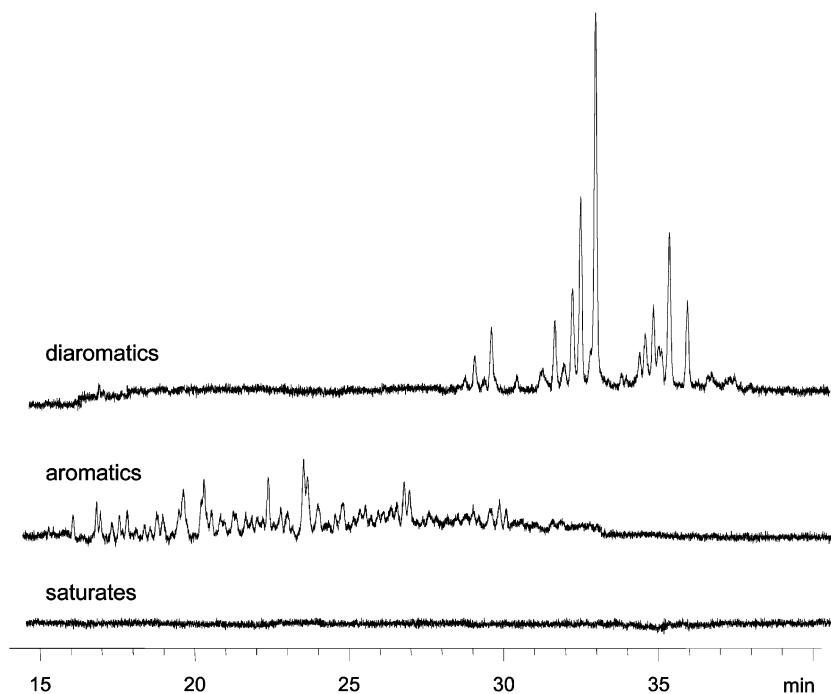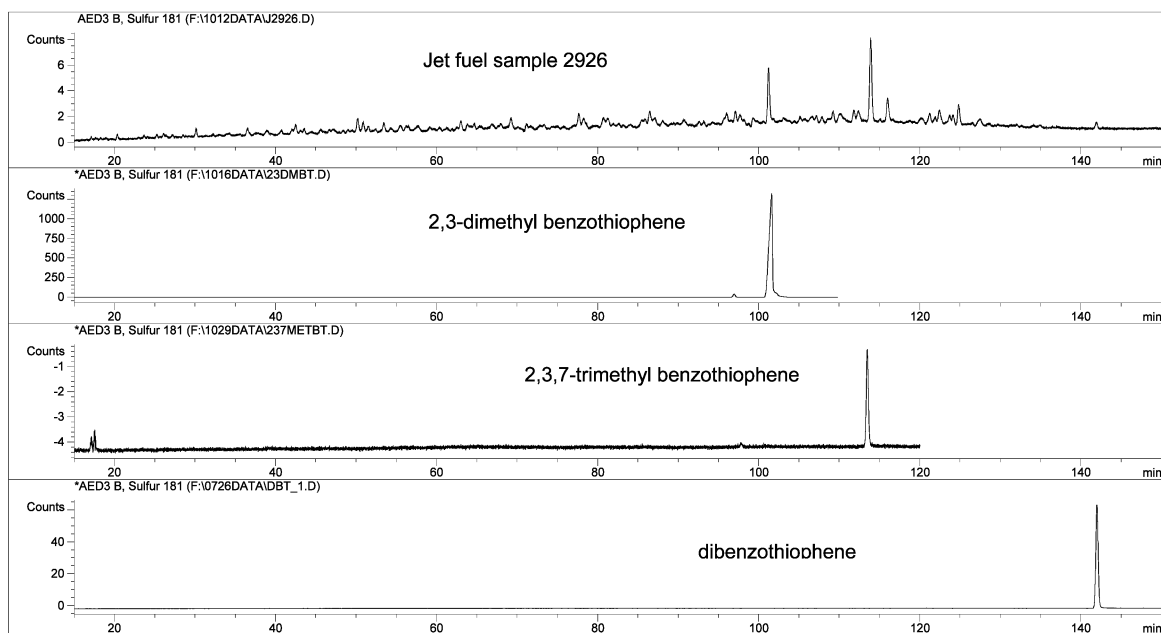
Figure 6. GC−AED sulfur chromatograms of the saturates, the aromatics, and the diaromatics following fractionation of the jet fuel by HPLC. All the extracted chromatograms are on the same scale.
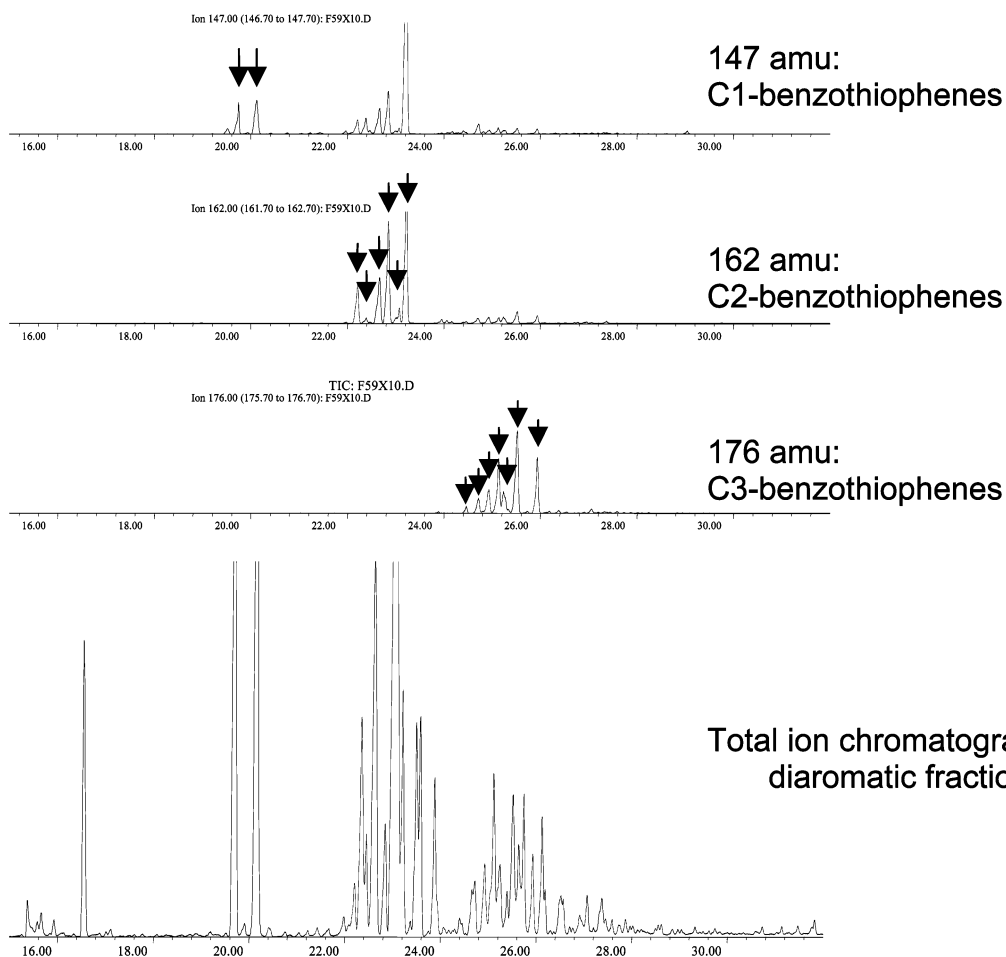
Figure 7. GC−MS analysis and identification of the sulfur components of the two-ring fraction of the jet fuel, as isolated by the HPLC fractionation procedure.

in the diaromatics fraction, as shown in Figure 6. Using masses that are indicative of specific groups of sulfur-containing compounds, group-specific identifications were made within each fractionated sample. This is shown in Figure 7, which identifies most of these sulfur compounds in the diaromatics fraction as alkyl-substi-

Figure 8. GC−AED sulfur chromatograms showing the identification of several sulfur-containing compounds in jet fuel by retention time matching.

tuted benzothiophenes. The fractionation step has the advantage of cleaning up the matrix prior to analysis, which allows for more-definitive identification of the trace amounts of sulfur-containing compounds in the bulk hydrocarbon matrix by mass spectrometric detection.

Identification of Individual Sulfur Constituents. Following the intensive separation of classes of sulfur compounds in the fuels, it was our goal to identify the individual compounds that comprised a majority of the classes. To do this, GC−AED sulfur chromatograms for jet fuels were compared to the results for solutions that contained a single sulfur compound. Identifications using this method were based on retention time matching. The major constituents of the alkyl-benzothiophene structures (C1, C2, and C3), and the major dibenzothiophene, were identified. Figure 8 shows the sulfur chromatogram of a representative jet fuel sample, as well as those of several components that were identified in the fuel: 2,3-dimethylbenzothiophene, 2,3,7-trimethylbenzothiophene, and dibenzothiophene. These identifications agree with other reports of sulfur compounds that are present in other fractions of hydrotreated fuels.[4,5,22,33]

Conclusions

This work has demonstrated effective techniques for separating aviation fuels into class-specific fractions to simplify the analysis of sulfur in the fuel and to quantify the reactive and nonreactive sulfur species in the fuel. Using these methods, fuels have been separated on the basis of the reactivity of the sulfur class, and on the basis of polarity and ring structure. The separation methods allowed a non-element-specific detection tech-

nique to be used, despite a large amount of matrix interference from the fuel. In addition, the separation methods increased the effectiveness of sulfur-specific methods such as gas chromatography−atomic emission detection (GC−AED).

Of the suite of sulfur-containing compounds in fuels, the thiols, sulfides, and disulfides are most reactive and were quantified by oxidation with either iodine or hydrogen peroxide, followed by the subtraction of bracketed regions of sulfur-specific chromatograms of the original fuel and the oxidized fuel. The least-reactive compounds—the thiophenes, benzothiophenes, and dibenzothiophenes—were also quantified by this bracketing and subtraction technique. However, the potential for losses of these compounds has been identified. The fuels tested in this study showed that reactive sulfur accounts for more than half of the sulfur concentration, which suggests that even a simple oxidation with hydrogen peroxide may greatly improve the fuel characteristics.

Using a high-pressure liquid chromatography fractionation technique, non-element-specific detection was used to establish that the class of fuel that contains the majority of sulfur is the diaromatics portion. Within this portion, sulfur exists primarily as alkyl-benzothiophenes, as determined by gas chromatography−mass spectroscopy, with individual contributors that are identified by GC−AED as being 2,3-dimethylbenzothiophene, 2,3,7-trimethylbenzothiophene, and dibenzothiophene.

(33) Ma, X.; Sakanishi, K.; Mochida, I. *Ind. Eng. Chem. Res.* **1996**, *35*, 2487−2494.